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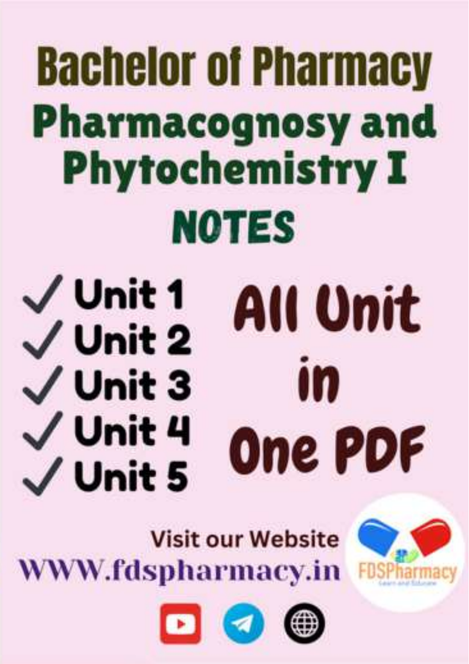
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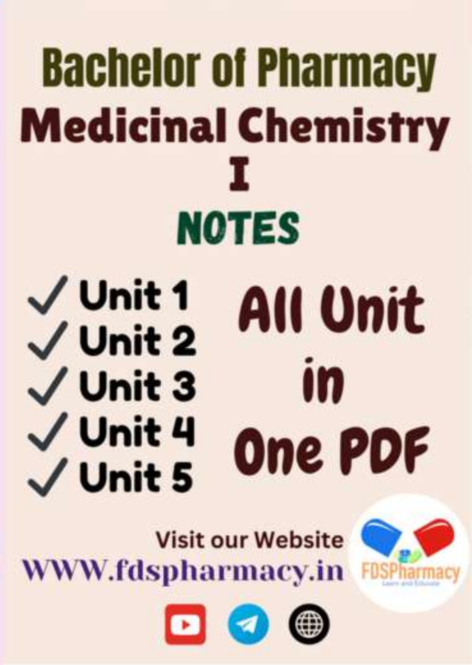
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PHYSICAL PHARMACEUTICS - II

UNIT 1

TOPIC :

- **Colloidal dispersions :** Classification of dispersed systems & their general characteristics, size & shapes of colloidal particles, classification of colloids & comparative account of their general properties. Optical, kinetic & electrical properties.
  Effect of electrolytes, coacervation, peptization& protective action.

Colloidal Dispersion

A colloidal dispersion is a heterogeneous system in which very small particles of one substance are uniformly distributed throughout another substance.

- The dispersed particles are not dissolved, but remain suspended due to their small size and continuous interaction with the dispersion medium.
- Particle size: 1 nm – 1000 nm.
- Phases of a colloid:
  - Dispersed phase: The substance that is distributed in the system.
  - Dispersion medium: The continuous phase in which particles are dispersed.

Classification of Dispersed Systems (Based on Particle Size)

Dispersed systems are classified into three types:

A. Molecular Dispersion (True Solutions)

- Particle size: < 1 nm.
- Nature: Homogeneous.
- Visibility: Particles are invisible even under an electron microscope.
- Diffusion: Rapid.
- Sedimentation: Do not settle down.
- Filtration: Pass through ordinary filter paper and semipermeable membranes.
- Examples: Salt solution, sugar solution.

B. Colloidal Dispersion

- Particle size: 1 nm – 1000 nm.
- Nature: Micro-heterogeneous (appears homogeneous to naked eye).
- Visibility: Not visible to naked eye but seen under electron microscope/ultramicroscope.
- Diffusion: Very slow.
- Sedimentation: Stable, may settle only under ultracentrifugation.

- Filtration: Pass through filter paper but not semipermeable membranes.
- Examples: Milk, fog, starch sol, blood plasma.

C. Coarse Dispersion (Suspensions/Emulsions)

- Particle size: > 1000 nm.
- Nature: Heterogeneous.
- Visibility: Particles are visible under optical microscope or even with naked eye.
- Diffusion: Do not diffuse.
- Sedimentation: Rapid, particles settle under gravity.
- Filtration: Separated by ordinary filter paper.
- Examples: Pharmaceutical emulsions, suspensions, muddy water.

Differences between Molecular, Colloidal & Coarse Dispersions

Property	Molecular Dispersion	Colloidal Dispersion	Coarse Dispersion
Particle size	< 1 nm	1 – 1000 nm	> 1000 nm
Nature	Homogeneous	Micro-heterogeneous	Heterogeneous
Visibility	Invisible even under electron microscope	Visible under electron microscope	Visible under optical microscope/naked eye
Diffusion	Rapid	Very slow	Do not diffuse
Sedimentation	Do not settle	Settle only under ultracentrifuge	Rapid sedimentation
Filtration	Pass through all filters	Pass through filter paper but not semipermeable membrane	Retained by filter paper
Examples	Salt solution, sugar solution	Milk, fog, starch sol	Emulsions, suspensions

Classification of Colloids

Basis of Classification

Colloids can be classified on two main parameters:

1. **Based on the state of dispersed phase and dispersion medium**
2. **Based on interaction between dispersed phase and dispersion medium**

Classification Based on Physical State of Dispersed Phase & Dispersion Medium

Dispersed Phase	Dispersion Medium	Type of Colloidal System	Examples
Solid	Solid	Solid sol / solid solution	Gemstones, alloys
Solid	Liquid	Sol	Paints, inks
Solid	Gas	Aerosol of solids	Smoke, dust in air
Liquid	Solid	Gel	Jelly, butter, cheese
Liquid	Liquid	Emulsion	Milk, cream, lotions
Liquid	Gas	Aerosol (liquid in gas)	Fog, mist, clouds
Gas	Solid	Solid foam	Foam rubber, pumice stone
Gas	Liquid	Foam	Shaving cream, whipped cream

Classification Based on Interaction Between Phases

A. Lyophilic Colloids (Solvent-loving)

- Strong affinity between **dispersed phase** and **dispersion medium**.
- Readily formed by direct mixing; highly stable.
- Reversible sols: if dried, can be reconstituted.
- High viscosity; show strong hydration.

- **Examples**: Starch in water, gelatin in water, cellulose derivatives.

B. Lyophobic Colloids (Solvent-hating)

- Little or no affinity between phases.
- Cannot be prepared directly; require special methods (e.g., electrical disintegration, chemical reactions).
- Thermodynamically unstable; easily coagulate on addition of electrolytes.
- Irreversible sols.
- **Examples**: Gold sol, sulfur sol, arsenic sulfide sol.

C. Association Colloids (Micelles)

- Formed by **surface-active agents (surfactants)** having both hydrophilic (polar) and hydrophobic (nonpolar) groups.
- At low concentration: exist as simple molecules.
- Above a characteristic concentration called **Critical Micelle Concentration (CMC)**, molecules aggregate to form **micelles**.
- Micelles behave as **colloidal particles**.
- Important in **detergency, drug delivery, and solubilization**.
- **Examples**: Sodium lauryl sulfate, soaps, detergents.

Properties of Colloids

The properties of colloids are broadly classified into three categories:

1. Optical Properties
2. Kinetic Properties
3. Electrical Properties

1. Optical Properties

Optical properties describe how colloidal particles interact with light – by scattering, absorption, fluorescence, or refraction. These properties are important for appearance, identification, and stability of colloidal systems.

a) Tyndall Effect

- Phenomenon in which a beam of light becomes visible when passed through a colloidal solution due to scattering of light by colloidal particles.
- Not observed in true solutions because their particles are too small.
- Examples: Sunlight through fog, headlights in mist.

b) Absorption of Light

- Colloidal particles selectively absorb light at particular wavelengths.
- Metal sols (gold, silver) show characteristic colors depending on particle size and wavelength absorbed.
- Example: Gold sol may appear red, blue, or purple.

c) Fluorescence

- Some colloids absorb light at one wavelength and emit it at another (longer) wavelength.
- This property is useful in analytical and diagnostic applications.

d) Opalescence

- Colloids often show a milky or pearly appearance due to scattering and interference of light.
- Seen in opals, milk, and some emulsions.

2. Kinetic Properties

Kinetic properties are related to the motion and behavior of colloidal particles due to their small size and interaction with dispersion medium.

a) Brownian Motion

- Random zig-zag movement of colloidal particles suspended in liquid or gas.
- Caused by continuous collisions with molecules of the dispersion medium.
- First observed by Robert Brown (1827).
- Helps prevent settling of particles and provides stability.

b) Diffusion

- Movement of particles from a region of higher concentration to lower concentration.
- Much slower in colloids compared to true solutions due to larger particle size.

c) Sedimentation

- Settling of colloidal particles under the influence of gravity or centrifugal force.
- Normal gravity is often insufficient; requires ultracentrifugation.

d) Viscosity

- Refers to the thickness or resistance to flow of a colloidal solution.
- Depends on particle size, shape, and concentration of dispersed phase.
- Lyophilic sols generally have higher viscosity than lyophobic sols.

3. Electrical Properties

Colloidal particles usually carry an electrical charge, which plays a crucial role in their stability.

a) Electrical Double Layer

- When a colloidal particle becomes charged, it attracts oppositely charged ions from the surrounding medium.
- This leads to the formation of two layers:
    1. Fixed layer: Ions firmly attached to particle surface.
    2. Diffuse layer: Loosely held counter-ions in surrounding medium.
- Together, these two layers form the Electrical Double Layer, responsible for repulsion and stability.

b) Zeta Potential

- The potential difference between the particle surface and the bulk dispersion medium.
- Indicates the degree of repulsion between particles:
    - High zeta potential → Strong repulsion → Stable colloid.
    - Low zeta potential → Weak repulsion → Particles aggregate → Coagulation.

c) Electrophoresis

- Movement of charged colloidal particles under the influence of an electric field.
- Positively charged particles → move toward cathode (–).
- Negatively charged particles → move toward anode (+).
- Used in separation techniques (e.g., gel electrophoresis in biochemistry).

Effect of Electrolytes on Colloids

- Colloids are heterogeneous systems where the dispersed phase has particle size between 1 nm to 200 nm.
- The stability of colloidal systems is mainly due to the electrical charge present on colloidal particles.
- When electrolytes are added, they can alter surface charge, reduce repulsion, and induce coagulation or flocculation.

Mechanism of Action of Electrolytes

1. **Ion adsorption**: Colloidal particles carry a charge due to selective adsorption of ions from the medium.
    - Example: In arsenic sulfide sol (As_2S_3), particles are negatively charged due to adsorption of S^{2-} ions.
2. **Electrical double layer**: A charged particle is surrounded by a fixed layer of counter-ions and a diffuse layer → together called Electrical Double Layer (EDL).
    - This EDL provides zeta potential (ζ) which maintains repulsion between particles and prevents aggregation.
3. **Addition of electrolytes**:
    - Electrolyte ions neutralize or compress the double layer.
    - As zeta potential decreases, repulsive forces weaken and particles come closer → leading to coagulation/precipitation.

Key Effects of Electrolytes

1. **Coagulation (Flocculation/Precipitation):**
    - When sufficient electrolyte is added, colloidal particles lose stability and aggregate.
    - Example: Arsenic sulfide sol coagulates in presence of $AlCl_3$.
2. **Electrolyte type matters:**
    - The ion carrying charge opposite to colloidal particles is responsible for coagulation.
    - Example: For negatively charged sol, cations cause coagulation.

3. **Valency rule (Schulze–Hardy Rule):**
    - Coagulating power of an ion is directly proportional to the fourth power of its valency.
    - Higher valency ions are more effective.
    - Example (for negative sol):
        - Na^+ (monovalent) < Ca^{2+} (divalent) < Al^{3+} (trivalent)
4. **Critical Coagulation Concentration (CCC):**
    - The minimum concentration of electrolyte required to cause coagulation.
    - Lower CCC → higher coagulating power.

Examples

- **Negatively charged sols** (e.g., As_2S_3 sol): coagulated by cations ($Al^{3+} > Ca^{2+} > Na^+$).
- **Positively charged sols** (e.g., $Fe(OH)_3$ sol): coagulated by anions ($PO_4^{3-} > SO_4^{2-} > Cl^-$).

Pharmaceutical Importance

- **Stability of colloidal drug suspensions** depends on controlling electrolyte concentration.
- **Parenteral colloids (IV emulsions, liposomes):** electrolytes may destabilize formulations.
- **Protective colloids (e.g., gelatin, acacia):** prevent coagulation by forming a protective film.
- Used in purification of colloids (dialysis and ultrafiltration to remove electrolytes).

Coacervation

- Coacervation is a process of phase separation in a colloidal system where a colloid-rich phase (coacervate) separates out from a colloid-poor phase.
- The coacervate is a dense, polymer-rich droplet formed due to reduction in solubility of colloids.
- In simple terms → colloidal particles aggregate and separate as a new phase while still dispersed in the medium.

Types of Coacervation

1. **Simple Coacervation**
    - Induced by adding a dehydrating agent or electrolyte to a colloid solution.
    - The solvent layer around colloid particles is removed → leading to phase separation.
    - Example: Addition of NaCl to gelatin solution.
2. **Complex Coacervation**
    - Occurs when two oppositely charged hydrophilic colloids interact and separate into two phases.
    - Example: Gelatin (positive charge at acidic pH) + Acacia (negative charge) → coacervate formation.

Mechanism of Coacervation

1. Reduction of solubility of colloidal particles (by salts, non-solvent, or polymer interaction).
2. Aggregation of colloid particles into larger clusters.
3. Formation of dense, colloid-rich droplets (coacervates).
4. Separation into two liquid phases:
    - Coacervate phase (rich in colloid)
    - Supernatant phase (poor in colloid)

Factors Affecting Coacervation

- **pH of solution** (affects ionization of colloids).
- **Electrolyte concentration** (salting out).
- **Temperature** (affects solubility and hydration).
- **Polymer charge density** (in case of complex coacervation).

Applications in Pharmacy

1. **Microencapsulation of drugs**
    - Coacervation is widely used to coat and entrap drugs in polymers.
    - Controlled and sustained release formulations.
    - Example: Encapsulation of oils, vitamins, and proteins.
2. **Taste masking**
    - Bitter drugs can be coated with polymers using coacervation.
3. **Protection of drugs**
    - Sensitive drugs (e.g., enzymes, probiotics) are protected from degradation.
4. **Parenteral and oral formulations**
    - Gelatin-acacia coacervates used for depot injections and slow-release capsules.

Examples

- **Gelatin + acacia system** → microcapsules for controlled drug release.
- **Ethyl cellulose coacervation** → taste masking of paracetamol.
- **Albumin coacervates** → sustained-release protein formulations.

Peptization

- Peptization is the process of converting a freshly precipitated substance into a colloidal sol by the addition of a small amount of electrolyte.
- The electrolyte added is called a peptizing agent.

Mechanism

1. Fresh precipitate has small particles with a tendency to aggregate.
2. When peptizing electrolyte is added, its ions are adsorbed on the surface of precipitate particles.
3. This adsorption imparts an electrical charge to particles.
4. The electrostatic repulsion prevents aggregation, and particles disperse → forming a stable colloidal sol.

Examples

- $Fe(OH)_3$ precipitate + small amount of $FeCl_3 \rightarrow Fe(OH)_3$ sol.
- $AgCl$ precipitate + $AgNO_3 \rightarrow AgCl$ sol.

Pharmaceutical Importance

- Used in preparation of colloidal sols of drugs and metals.
- Helps in redispersion of precipitated suspensions.
- Important in colloidal formulations where particle size control is needed.

Protective Action of Colloids

- The ability of lyophilic colloids (like gelatin, acacia, starch, gums) to protect lyophobic colloids (like gold sol, arsenic sulfide sol) from coagulation by electrolytes.
- Such lyophilic colloids are called protective colloids.

Mechanism

1. Protective colloids form an adsorbed layer around lyophobic particles.
2. This adsorbed layer prevents direct contact of lyophobic particles.
3. Even when electrolyte is added, the lyophilic coat resists coagulation → stabilizing the colloidal system.

Example

- Gold sol is stabilized by gelatin → basis of Gold Number test.